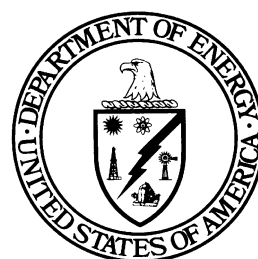


Laser Ablation Mass Spectroscopy (LA/MS)

Tanks Focus Area



Prepared for
U.S. Department of Energy
Office of Environmental Management
Office of Science and Technology

September 1998

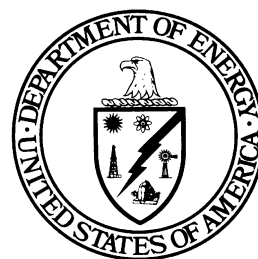
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Laser Ablation Mass Spectroscopy (LA/MS)

OST Reference # 127

Tanks Focus Area



Demonstrated at
U.S. Department of Energy
Hanford Site
Richland, Washington



Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine if a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at <http://ost.em.doe.gov> under "Publications."

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SECTION 1

SUMMARY

Technology Summary

Laser Ablation/Mass Spectroscopy (LA/MS) is a chemical analysis method that can determine the amount of most elemental/isotopic constituents in tank waste samples with no sample preparation. It provides elemental and/or isotopic detection and quantification of most elements in the periodic table. This technology has the potential to provide rapid analytical results while lowering production times and worker exposure.

How it Works

A pulse laser beam is used to remove very small amounts of material from a tank waste sample; this process is called laser ablation. The inert carrier gas (argon) transfers the ablated sample to the inductively coupled plasma torch. Here, the sample plume is disassociated into atomic species and the atoms are ionized. Then, the ionized atoms enter the mass spectrometer and are analyzed to determine the number of atoms at each atomic weight. The resulting data set, or particle count at each mass number, directly indicates the elemental and isotopic species and their populations in the sample. Figure 1 shows the components of the Laser Ablation/Mass Spectrometer system.



Figure 1. Laser Ablation/Mass Spectrometer (LA/MS) system showing in-cell equipment, operator with manipulator, fume hood, and electronics.



Advantage Over Baseline

Routine use of the LA/MS method for sample analyses can result in significant cost, time, and worker exposure reductions when compared to baseline analysis methods which include: (a) inductively coupled plasma/atomic emission spectroscopy (ICP/AES) for the elemental analysis of dissolved samples, and (b) radio-analytical methods which often require the performance of chemical separations before analysis.

- LA/MS analysis has suitable sensitivity and dynamic range to provide data on constituent concentrations ranging from parts-per-million (ppm) to tens of percent with a single analysis.
- The LA/MS method offers higher analytical laboratory throughput than baseline methods under high work load conditions.
- Baseline processes routinely require the removal of radioactive materials from the hot cells for dissolution, preparation, and analysis resulting in staff radiation exposures which can be further reduced by using the LA/MS method.
- The LA/MS system may significantly reduce the secondary waste generated by baseline methods.

Potential Markets

The LA/MS method is applicable for a broad range of solid material analyses including radioactive materials in the U.S. Department of Energy inventory (including tank waste) and non-radioactive materials encountered in environmental clean-up and industrial applications. Potential LA/MS applications include opportunities at a variety of DOE sites including Hanford, Savannah River, Oak Ridge, and Idaho National Engineering and Environmental Laboratory.

Demonstration Summary

A LA/MS analytical system was demonstrated in a Hanford analytical laboratory (222-S) hot cell in 1996. This report covers work funded by EM50/TFA in the period 7/95 – 12/97 and the results of complimentary work funded by the EM30/TWRS (Tank Waste Remediation System) Characterization Program in the period 10/92 – 9/96. Collaborators in FY96 during the design and deployment of the LA/MS system included staff from the Westinghouse Hanford Co. and the ICF Kaiser Hanford Co.

Inherent in the fast track deployment plan (15 months from commitment to demonstration) was the recognition that interim versions of control and data reduction software would be demonstrated at the end of FY96. Since its deployment, the system has been used to analyze waste from Tank U-105 and a number of Hanford reactor basin sludge samples.

Key Results

- Analysis of the LA/MS data provided semi-quantitative elemental concentration values which were generally consistent with results of previous sample analyses.
- The hot cell LA/MS system provided rapid, effective analyses for major, minor, and trace constituents in tank waste samples.
- LA/MS results were generally consistent with findings from previous waste characterization using baseline analytical methods.
- During the hot cell demonstration, the time for data acquisition and preliminary data analysis to determine major, minor, and trace waste constituents was less than 6 hours and results were reported within 2 working days. This is significantly faster than the baseline method analysis times of approximately 30 days for normal processing and approximately 6 – 8 days for priority processing.
- The LA/MS demonstration data for Tank U-105 waste show the value for rapid waste classification screening. The waste classification information can be used to guide the development of detailed analysis plans for waste samples.



Specific near-term and long-term DOE applications where LA/MS methods offer advantages for rapid chemical analysis to support TWRS activities include:

- Characterization: Analysis of core, subcore, and composite samples to determine elemental/isotopic constituents and homogeneity.
- Development of robust processes and equipment for retrieval, pretreatment, and immobilization of tank waste materials.
- Support of production waste processing: a) On-line analysis of pilot Pretreatment Plant feed and product, and. b) On-line analysis of vitrification plant feedstock and final glass product.

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Other

All published Innovative Technology Summary Reports are available on the OST Web site at <http://em-50.em.doe.gov> under "Publications." The Technology Management System, also available through the OST Web site, provides information about OST programs, technologies, and problems. The OST Reference # for Laser Ablation/Mass Spectroscopy is 127.



SECTION 2

TECHNOLOGY DESCRIPTION

Overall Process Definition

LA/MS provides data on the majority of waste material constituents.

- The LA/MS system can detect more than 80 elements at sub-ppm concentrations. Ten of these are major oxides in tank wastes, while six are noble metals. Twenty of the elements detected at sub-ppm levels are radioactive isotopes.
- Five elements can be detected at sub-percentage levels, including carbon, phosphorous, sulfur, chlorine, and potassium.

Figure 2 provides an overview of the elemental detection sensitivity estimated for the LA/MS during analysis of Hanford tank waste materials. The ability of the LA/MS method to provide data on the majority of waste material constituents is apparent. Elements that can not be determined using an argon carrier gas and argon ICP are noted.

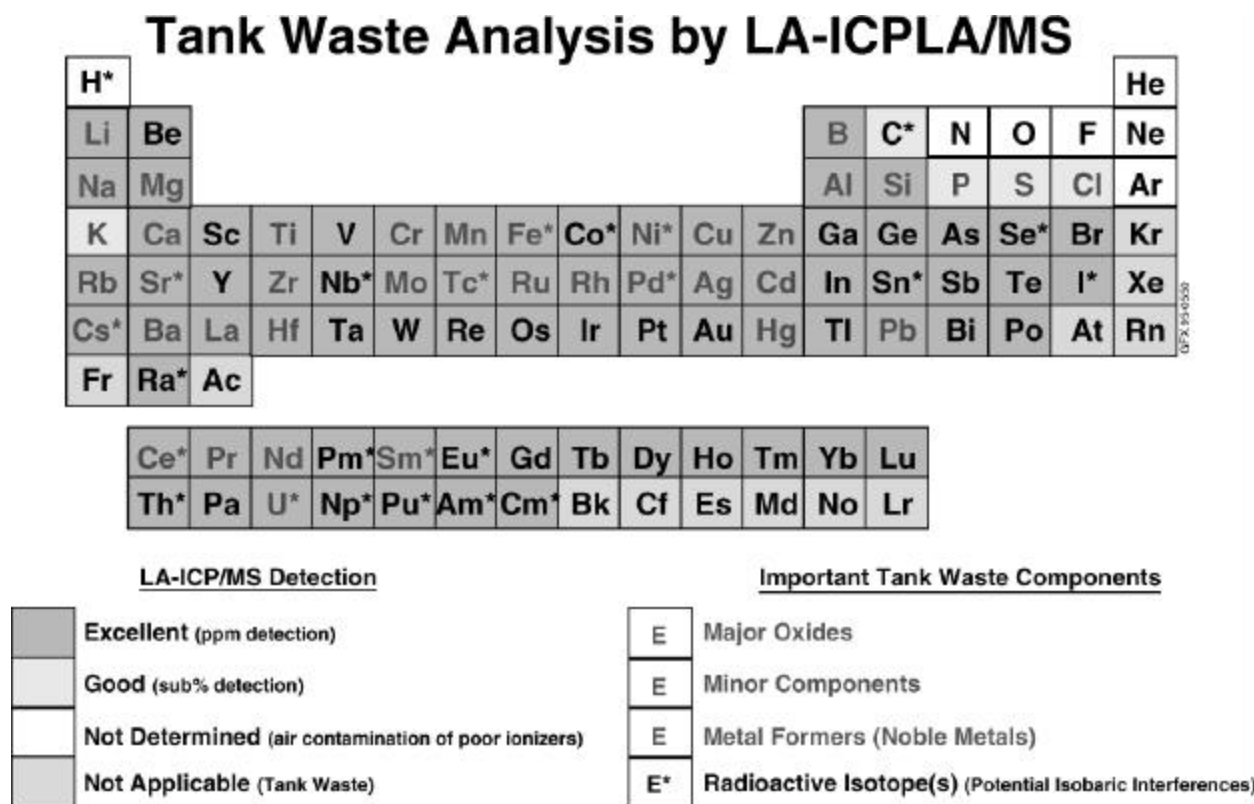


Figure 2. Periodic table of the elements with projected LA/MS method detection capability.

As shown in a simplified system representation in Figure 3, LA/MS system components include:

- an ablation laser,
- an optical system for transferring and focusing the laser beam,
- a sample chamber with translation stages,
- an ablation plume pickup and transfer line to transport the plume to the ICP/MS,
- an inductively coupled plasma (ICP),

- a mass spectrometer (MS), and
- a video system to aid the operator in system operation and maintenance.

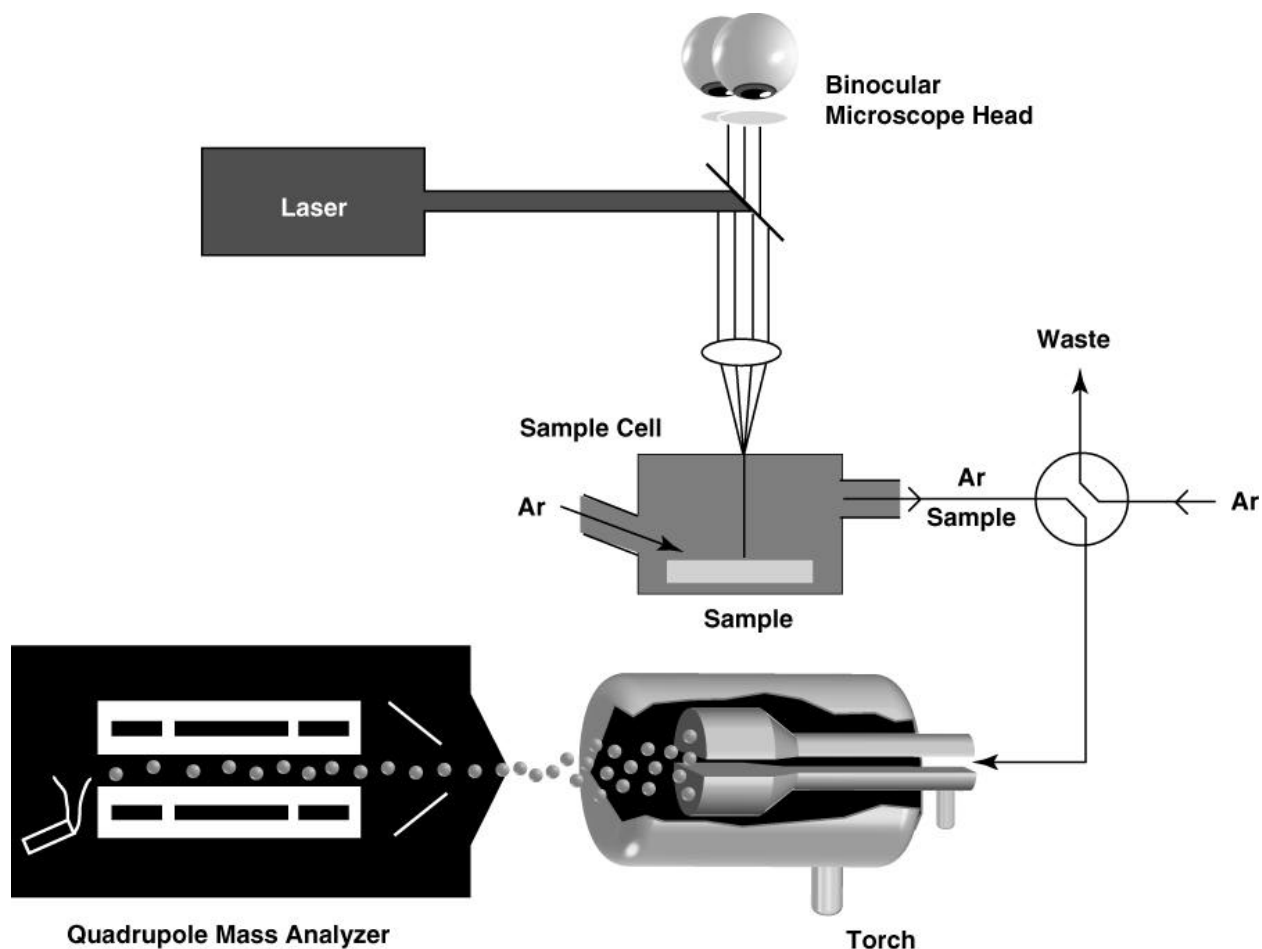


Figure 3. Schematic of the LA/MS system configuration and key components.

In the LA/MS system configuration in the 222-S laboratory, the LA/MS hot cell is the last cell in a group of four interconnected hot cells. Sample extrusion and placement in the LA/MS sample holder takes place in the cell opposite of the LA/MS hot cell. The sample is transferred to the LA/MS system using a transfer cart operating in a shielded connecting tunnel. The system's optical source is located on the hot cell roof; the laser beam is transferred through a roof penetration to the sample. The source assembly and beam path enclosures have safety interlocks to allow operation as a Class I laser system. In-cell components are limited to the final optics, sample holder, sample translation stages, and ablation plume pickup. All are operable and maintainable using manipulators. The ICP/MS instrument is located in a dual fume hood next to the hot cell to simplify instrument adjustment and maintenance. Auxiliary electronics equipment is located on the hot cell roof (under the optics table), adjacent to the fume hood, and adjacent to the operator console.

System Operation

Prior to analysis the sample must be prepared. The sample preparation and analysis sequence is summarized below.

- Small waste subsamples (either after homogenization and/or compositing or directly from a core) are loaded into LA/MS system sample holders in the hot cell.
- A reference sample is placed in the sample holder adjacent to the waste sample.
- The loaded sample holders are transferred to the LA/MS cell using an electric cart.

- The sample holders are placed on the LA/MS system translation stage bracket using manipulators.
- Following system set-up, the sample holders (with waste and reference samples) are moved through a prescribed scanning pattern under the laser beam to ablate material from a region of the sample.
- ICP/MS data for the ablated plume material are integrated to provide raw MS data from the scanned surface area (area averaging of the constituents).
- Background MS data are recorded with NO laser beam incident on the sample surface.
- Replicate data sets are recorded for the background, reference, and waste sample.
- Complimentary system operating data are recorded simultaneously by the system computer.
- Integrated data files are transferred to the data reduction computer to allow data processing while the next sample is being loaded and analyzed.

LA/MS system operation is a simple process where the ablation laser produces a pulse of optical energy that strikes the sample surface. The laser pulse interacts with the sample material, causing a small plume of material to be ablated from the sample (typically nanograms of sample material per laser pulse). Next, the plume is entrained in a gas flowing over the sample and carried into the transfer line. This carrier gas transports the plume material from the sample into the ICP. The plasma vaporizes and dissociates plume particles into atoms and ionizes the atoms. Finally, the ions enter the MS and are analyzed to determine the quantity at each mass number.

Typical operating parameters and conditions are listed below.

- Laser: Beam diameter at sample approximately 50 micrometers; approximately 0.1 – 0.2 mJ/pulse; 6 nanosecond pulse duration; 20 pulses/second; 226 nm or 355 nm wavelength.
- Sample area scanned for data sets: 2 mm x 2 mm.
- Integration time for individual MS data sets: 45 seconds (i.e. 900 laser pulses)
- Sample cover and plume transfer gas: Argon

Staff Training

An analytical chemist or technical specialist can perform system operation. With current software, a chemist must perform data reduction and analysis. When data reduction improvements are implemented, technical specialists can perform much of the preliminary processing with final interpretation by a chemist.

Waste Streams

LA/MS analysis will significantly reduce waste streams compared to baseline analysis methods. No sample dissolution is required for LA/MS analysis, eliminating significant secondary waste generation including unused solutions and glassware employed during the baseline sample preparation processes. Airborne particulates from the ablation plume are removed using standard HEPA filters.

Potential Operating Concerns

None. System design resolved operating concerns, including laser and radiation safety issues. Required permits are in place, and safe operation has been demonstrated.



SECTION 3

PERFORMANCE

Demonstration Plan

Tests that demonstrated the LA/MS analytical capability were first conducted using a LA/MS system with a fume hood enclosure. This system analyzed waste from Tanks S-104, T-104, and T-111. When the hot cell system was designed and installed, system demonstration was successfully completed using waste from Tank U-105. The objectives of the deployment were to demonstrate:

- a rapid method of chemical analysis of major, minor, and trace elemental constituents in a solid radioactive waste tank sample, and
- operation of the integrated hot-cell LA/MS system including major analytical subsystems, ancillary instrumentation, computer-based system controls, the data acquisition system, and data reduction.

The LA/MS analytical method was initially demonstrated on radioactive TWRS waste samples (See Table 1) using a PNNL laboratory fume hood LA/MS system, rather than a hot-cell deployed system. Samples received from each tank included a "raw" sample (i.e., no treatment beyond core extrusion, subsampling, and homogenization) and a "pretreated" sample. The pretreated samples had been "washed" in an effort to remove soluble analytes, which were left in the waste following removal from the tanks and extrusion in the hot cell. The sample materials had been previously analyzed using baseline and those data were available to aid in evaluating these preliminary LA/MS results for actual waste samples (Rapko 1995).

Table 1. Summary information for tank waste samples analyzed using fume hood LA/MS instrumentation system

<u>Hanford Tank</u>	<u>Waste Description</u>
Tank S-104	A primary waste product from the reduction oxidation (REDOX) process
Tank T-104	A first-cycle decontamination waste from the bismuth-phosphate process
Tank T-111	A second-cycle decontamination waste from the bismuth-phosphate process

These samples were chosen to provide representative sludge samples. Specifically, these samples were known to have a broad number of chemical constituents including heavy metals and radionuclides on the basis of prior independent analytical results (ICP/AES and radiochemistry analysis).

For the hot-cell demonstration, analysis was conducted using a sample from Tank U-105 (See Table 2). The U-105 sample material was previously homogenized, subsampled for prescribed analyses, and the unused portion was archived in a glass container. Results from the previous analysis are reported in Fritts (1996). Prior to LA/MS analysis, the material in the storage jar was stirred to re-homogenize the waste. The amount of waste placed in the LA/MS sample cup was estimated to be approximately 0.2 grams. LA/MS data for the U-105 sample was recorded on September 28, 1996. Preliminary analysis of the LA/MS data, including letter reports, were completed on September 30, 1996.



Table 2. Tank U-105 sample information

Hanford Waste Tank	U-105
Core/Segment (Portion)	136/9A (Upper Half)
Date Sampled	3/18/96
Date Extruded	4/3/96
Date of LA/MS Analysis	9/26/96
Description	Dark brown sludge

Subsequent data analysis was performed in early FY97 to provide semi-quantitative results from the U-105 data.

Results

Comparison of the results of the analysis of Hanford tank samples using the hot cell LA/MS system and using a laboratory fume hood LA/MS system were previously reported (Smith 1996). Key findings show:

- Analysis of the LA/MS data using preliminary data reduction protocols available in late FY96, provided semi-quantitative elemental concentration values that were generally consistent with results of previous sample analyses.
- The hot cell LA/MS system, (using the operational procedures employed for the FY96 demonstration) provided rapid, effective analyses for major, minor, and trace constituents in tank waste samples.
- LA/MS results were generally consistent with findings from previous waste characterization using baseline analytical methods.
- U-105 waste analysis determined major waste matrix constituents in the low mass range with fission products, lead, bismuth, and actinide elements representing significant waste components at higher mass values.
- Data exhibited both natural components and radiogenic products.
- Raster scanning of the sample beneath the laser beam to provide area averaging of sample constituents provided data that included the desired compositional averaging needed to obtain effective sample composition knowledge.
- Comparison of LA/MS analysis results for raw and washed waste samples from Tanks S-104, T-104, and T-111 demonstrated the LA/MS capability to rapidly identify elemental constituents that were removed from the waste material by the washing processes.
- During the hot cell LA/MS system demonstration, the elapsed time for data acquisition and preliminary data analysis to determine major, minor, and trace waste constituents was less than 6 hours and results were reported to EM50/TFA and EM30/TWRS project oversight staff within 2 working days. This demonstrated very rapid analysis when compared to the 222-S laboratory baseline method analysis times of approximately 30 days for normal processing and approximately 6 – 8 days for priority processing.
- Subsequent data reduction method and software development, which is being performed under the on-going TFA LA/MS, is nearing operational status and should further reduce LA/MS data reduction time required to obtain semi-quantitative sample composition to approximately 2 – 4 hours.

The raw mass spectra recorded for the U-105 waste sample is shown in Figure 4. The mass spectrometer data (vertical axis) correspond to an analyte concentration range from 10's of percent for major constituents to 10's of ppm for trace constituents. Major waste matrix elements are seen at low mass numbers while significant peaks are seen at higher masses due to fission products, lead, bismuth,



Analysis of the Tank U-105 data, using reference sample data (with a limited number of elemental constituents) and scaling estimates for the total mass spectrometer signal levels provided elemental concentration estimates. These data are shown in Figure 5, along with data from the baseline 222-S laboratory analysis of the U-105 material (ICP/AES analysis of a dissolved sample). The two data sets exhibit good agreement.

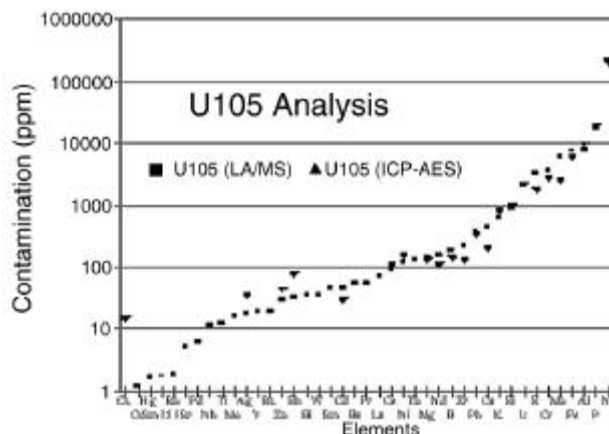


Figure 5. Elemental concentration levels for U-105 waste sample using ICP/AES analysis, and estimated LA/MS data (in order of increasing concentration).

SECTION 4

TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing Technologies

Discussion of competing technologies is limited to methods that can meet similar functional requirements to those met by LA/MS technology (specifically the analysis of solid sample materials) and that provide concentration data for a range of elemental constituents.

Baseline Technology: Solid sample analysis with methods requiring sample dissolution

The baseline elemental analysis methods for solid tank waste material employs solid sample dissolution followed by analysis of the solution sample using one of several analytical methods. The baseline analysis method is based on inductively coupled plasma/atomic emission spectroscopy (ICP/AES). Alternatively, inductively coupled plasma/mass spectrometry (ICP/MS) can be used to perform analysis of the solution containing the dissolved sample.

Both techniques are similar with respect to the excitation source, analysis time, ability to provide quantitative results, and cost. ICP/AES provides elemental data while ICP/MS provides mass specific data that can be interpreted to obtain elemental information using isotopic abundance assumptions/models. The ICP/MS technique is similar to the LA/MS because the detector is a mass spectrometer, however, the ICP/MS can only be used for liquids (including dissolved solid samples) or gases. The LA/MS extends the capabilities of the ICP/MS for complete analysis of solid samples.

Laser Ablation / Mass Spectrometer (described in Section 2)

Advantages commonly cited include:

- system built using commercially available and supported subsystems,
- very rapid analysis and potential for high throughput,
- measurement of a major portion of the elements in the periodic table from a single measurement,
- high measurement sensitivity (ppm level or better for most elements),
- high dynamic range (6 – 8 orders of magnitude),
- no sample preparation required (except homogenization of desired), and
- minimal secondary waste generated.

Disadvantages commonly cited include:

- cost of ICP/MS instrument subsystem, and
- very small amount of sample material must be transferred to the ICP/MS for analysis.

Laser-Induced Breakdown Spectroscopy

A Laser-Induced Breakdown Spectroscopy (LIBS) analysis system combines equipment elements found in both the LA/MS system (intense pulsed laser source) and the conventional ICP/AES system (optical spectrometer) to provide sample analysis. The laser provides high instantaneous power laser pulses which are directed to the sample surface. Sufficient laser intensity is employed to produce a small plasma near the sample's surface that vaporizes a small amount of sample material. The vaporized sample material is dissociated and the free atoms are ionized. Optical emissions result when the ions in the plasma region recapture free electrons and the electrons fall to low energy states in the atoms. The emission wavelengths are characteristic of the elements in the sample. The optical emissions are analyzed using an optical spectrometer in the same manner as employed for AES analysis.

Advantages commonly cited for LIBS analysis include:



- simple equipment design (laser source, transfer optics, plasma emission collection and transfer optics, optical spectrometer, control and data analysis system);
- operable in open atmosphere (no special cover gas requirements);
- can be designed for portable operation;
- relatively low cost compared to some methods (optical spectrometers are cheaper than mass spectrometers);
- the LIBS analysis requires no transfer of material from the sample to the detector (in contrast to a mass spectrometer-based analysis system). This may be significant for the analysis of radioactive sample materials.

Disadvantages commonly cited for LIBS include:

- lower data precision than some analysis methods;
- lower measurement/detection sensitivity than for mass spectrometer based methods;
- interpretation may be complicated by interferences between emission lines from different sample constituents;
- detectable element suite is reduced from typical ICP/AES (plasma interference and optical decay modes in the atmosphere) and much less than for mass spectrometer based methods; and
- LIBS is more destructive of the sample than LA/MS due to the use of higher laser pulse energies and the formation of useful plasma at the sample surface.

XRF Analysis

XRF analysis utilizes X-rays to excite inner shell electrons in atoms. Following excitation, the atoms emit X-rays with energies characteristic of the emitting atom/element. Analysis of the X-ray energy spectrum emitted from a sample can be used to establish the presence and quantity of a number of elemental constituents.

Advantages commonly cited include:

- non-contact, in-situ measurement,
- fairly rapid data acquisition and analysis,
- no material transfer required for analysis, and
- typical sensitivity of 1 ppm for elements with atomic numbers greater than 20.

Disadvantages commonly cited include:

- poor performance for low atomic number elements
- use of an X-ray source that brings associated radiation safety requirements/restrictions,
- interpretation may be complicated by interferences between emission lines from different sample constituents, and
- high resolution instruments require cryogenically cooled detectors.



Technology Applicability

The specific DOE application targeted for this demonstration was the analysis of solid, radioactive tank waste materials for elemental composition. Other possible DOE applications include:

- analysis of LLW and HLW solid samples resulting from waste treatment processing (e.g., sludge washing, waste vitrification, etc.) and
- rapid on-line analysis of vitrification plant feedstock solids and final glass product.

In addition, the LA/MS analysis method offers the advantage of rapid, broad elemental analysis for a broad range of non-DOE applications including:

- industrial sample characterization and product quality control and
- environmental site characterization and remediation validation.

There are no outstanding scale-up requirements for the basic LA/MS system equipment either for other DOE applications/sites or for non-DOE applications. System operating conditions (e.g., laser pulse energy) may need to be revised for different applications, but the system design provides the capability to easily make these adjustments using system controls. Specialized system engineering will probably be needed for certain applications to meet requirements for sample throughput or sample handling criteria (e.g., special equipment enclosures for carcinogens, radioactive materials, etc.).

Potential LA/MS applications include opportunities at a variety of DOE sites including Hanford, Savannah River, Oak Ridge, and Idaho National Engineering and Environmental Laboratory.



SECTION 5

COST

Methodology

The LA/MS system deployment and operational cost are compared to the costs of existing baseline analysis methods.

- Deployment cost figures are based on the FY96 multi-contractor team experience for deployment of the hot cell LA/MS system in the Hanford 222-S laboratory.
- Equipment costs are based on vendor discussions and the system configuration employed for the 222-S installation.
- 222-S analytical laboratory staff have provided baseline analytical service costs.

Cost analyses are based on laboratory cost/time estimates for individual process steps for a baseline method providing broad elemental constituent data (ICP/AES) and for the LA/MS analysis method. Cost/time information used for the analysis include: a) hot cell sample preparation and baseline analysis data from staff in PNNL's Analytical Chemistry Laboratory and in the 222-S laboratory and b) estimates for LA/MS system operation from PNNL LA/MS project staff.

Comparable times for data reduction, quality checks, and reporting were assumed, even though significant advantages are anticipated for the LA/MS method after completion of data reduction methods currently being developed. Unproven advantages for the advanced LA/MS data reduction methods have not been built into the estimates but could be incorporated following successful demonstration.

Cost Analysis

Cost estimates for deployment of integrated LA/MS instrumentation systems at other DOE sites and for applications other than the tank waste characterization depend on site and application-specific characteristics. In order to provide baseline information, costs associated with the FY96 deployment at Hanford are detailed in several categories. Site specific adjustments from the FY96 Hanford figures would need to be evaluated to obtain representative figures for individual applications.

Capital equipment costs for the LA/MS system at Hanford were approximately \$675K (See Table 3). Equipment costs for a new application will depend on application specific requirements that may include: ICP/MS containment in a glove box (as compared to the fume hood employed at Hanford); reduced auxiliary instrumentation suite as compared to the full suite employed at Hanford. Site requirements will govern the actual cost.

Table 3. Equipment cost estimates

Capital Equipment Costs	Estimated 222-S System Cost
Mass spectrometer without enclosure	\$ 225K
Fume hood or glove box enclosure design and fabrication	\$ 175K
Basic system equipment (less mass spectrometer)	\$ 220K
Equipment cost for basic system including fume hood (subtotal)	\$ 620K
Auxiliary system equipment (Not required for basic operation)	\$ 55K
Total cost for fully instrumented system with mass spectrometer and enclosure	\$ 675K

New design and deployment labor cost estimates will depend heavily on new application and site requirements (see Table 4). For example, if the application will involve the deployment of a standalone system in a large new work area, then limited facility modification and interface design efforts may be required. Whereas, if the LA/MS system will be installed in an existing operational hot cell facility, then



significant instrument system design (to meet available space and/or configuration requirements), facility design and modification, and installation costs must be considered.

Table 4. Estimated labor costs for system deployment

Labor Categories	Estimated 222-S System Cost
Instrument system design	\$ 145K
Facility design and modification (including all utility and supporting equipment installations required for instrument connections at time of deployment)	\$ 350K
Instrumentation installation and checkout	\$ 100K

The FY96 Hanford demonstration required the analysis of a single sample using the LA/MS system. Costs for demonstration at another site will be governed by the scope of the demonstration specified. The estimated system cost for a system demonstration following installation is \$10K. This would include the labor for sample handling, LA/MS data collection, and data reduction and analysis.

Table 5 compares the process steps for the baseline method and the LA/MS system. For the baseline method, Steps 4, 6, 7, and 8 are performed with subsample volumes being handled by laboratory staff outside the hot cell. In contrast, the LA/MS method is conducted with only a very small amount of sample material (i.e., the ablation plume) leaving the hot cell (Step 8) and it is transferred (without operator handling) via the carrier gas. Implementation of the LA/MS method can further reduce worker radiation exposure levels.

Table 5. Sample analysis process steps and their usage for selected analysis methods

Process Step	Step Number (for reference to plots)	Baseline Method ICP/AES Analysis of Dissolved Sample	LA/MS Analysis of Solid Sample
Core Extrusion	1	Y ⁽¹⁾	Y ⁽¹⁾
Visual Inspection/Sampling	2	Y ⁽¹⁾	Y ⁽¹⁾
Homogenization	3	Y ⁽¹⁾	Optional ⁽¹⁾ (Can directly examine core strata subsample)
Homogenization Check	4	Optional ⁽²⁾	N
Composite Preparation	5	Generally Employed, but Optional ⁽¹⁾	Optional ⁽¹⁾
Sample Fusion	6	Y ⁽²⁾	N ⁽¹⁾
Sample Preparation	7	Y ⁽²⁾	Y ⁽¹⁾
Sample Analysis	8	Y ⁽²⁾	Y ⁽³⁾
Data Reduction	9	Y ⁽²⁾	Y ⁽²⁾
Support Tasks	10	Y ⁽²⁾	Y ⁽²⁾

⁽¹⁾ Operation performed in hot cell.

⁽²⁾ Operation performed outside hot cell.

⁽³⁾ Operation performed with sample in hot cell and small ablated plume transferred to ICP/MS in attached fume hood.

In the baseline method, Steps 3 – 5 can be very labor intensive and time consuming depending on the detailed process step methods employed.

- Sample homogenization, when performed with a double planetary mixer takes up to 4 hours.
- The homogenization check, when performed with the baseline method, entails subsample dissolution with analysis following Steps 6 – 9, requires approximately 12 labor hours, has an elapsed time of up to 40 hours, and provides a sample throughput rate of 0.1 sample every 4 hours. (It should be noted that LA/MS offers a real opportunity to provide rapid, low cost verification of homogenization by taking small subsamples from the homogenized material for LA/MS analysis.)



- Composite preparation takes approximately 8 labor hours to prepare a proportional mix from segment subsections and homogenize the combined mixture.

Due to the variations possible in process steps 1 – 5 for the two analysis methods, the following comparisons have been conducted by evaluating Steps 6 – 10 which are common to both methods under all circumstances. Comparative plots that summarize the findings follow. As noted above, inclusion of labor and elapsed times in the baseline method for Steps 1 – 5 would further extend the labor costs and elapsed time for the baseline method.

Figure 6 shows the labor hours for the two analysis methods for process Steps 6 – 10 (solution analysis on left and LA/MS on right). The solution-based analysis requires more labor for Steps 6, 8, and 9 while the LA/MS requires more time for Step 7. It has been assumed that both methods will require the same effort for support activities (Step 10). Figure 7 illustrates the cumulative for the two analysis methods. Note that through the completion of the data reduction, the LA/MS method requires about 68 percent less labor than the solution-based analysis.

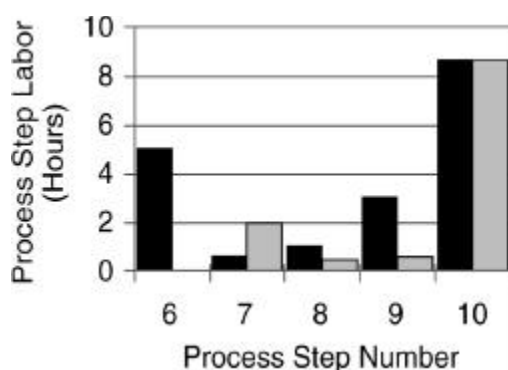


Figure 6. Labor hours for process steps.

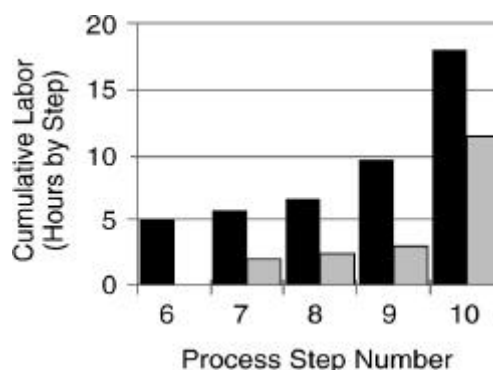


Figure 7. Cumulative labor hours through process step.

Figure 8 illustrates the elapsed time for performance of the individual process steps for the two analysis methods. Sample fusion (Step 6) clearly requires the most time of any of the process steps. Figure 9 illustrates the cumulative elapsed time for the two analysis methods. Note that through the completion of the data reduction, the LA/MS method requires less than 20 percent of the elapsed time for the solution based analysis. In time of low laboratory workloads, the cumulative elapsed time establishes a practical limit for sample turn around time. During periods of high laboratory backlogs, the process step with the lowest throughput rate will govern the rate that samples can be processed. In this case, sample turn around time can be estimated from the sample backlog and the lowest step throughput rate. For this analysis, it has been assumed that support tasks (Step 10) will be the same for both methods.

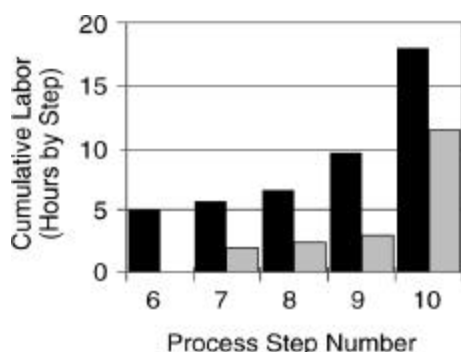


Figure 8. Execution time for each process step.

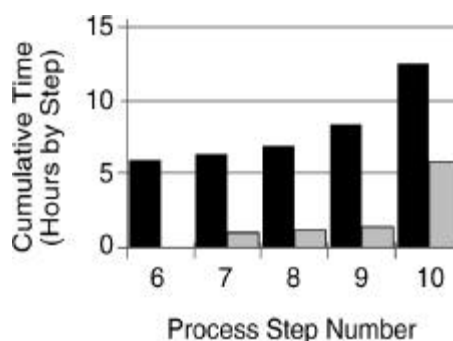


Figure 9. Plot of cumulative execution time through process step.

Figure 10 illustrates the throughput rate for each process step for the two analysis methods. Based on these data, it would be expected that the LA/MS method could support sample throughput rates roughly five times greater than for the solution based analysis method.

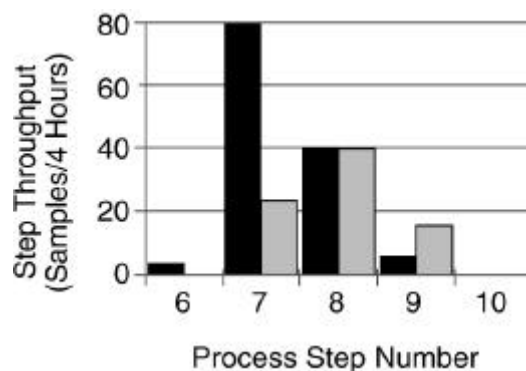


Figure 10. Process step throughput rates.

Estimates of comparative operating costs are shown in Table 6 for one baseline method (dissolved solid analysis by ICP/AES). The LA/MS method (also shown) has been prepared for two analysis options: a full process sequence (Steps 1 – 10) and a partial process sequence (Steps 6 – 10). A staff labor charge out rate of \$60/hour has been used for the calculation (FY96 Hanford M&O contractor rate for analytical services). The annual savings estimate is based on the assumption of full quantitative LA/MS analysis capability at 222-S, which is planned for operation in FY98.

Table 6. Estimated annual operating costs for baseline and LA/MS analyses based on FY96 Hanford lab labor rates and estimated sample throughput of 2000 samples/year*

	Full TWRS Characterization (Steps 1 – 10)		Pretreated Sample Characterization (Steps 6 – 10)	
	ICP Solution	LA/MS	ICP Solution	LA/MS
Homogenization	\$540	\$0	\$0	\$0
Costs	\$3450/sample	\$540/sample	\$740/sample	\$540/sample
Total Costs	\$3990/sample	\$540/sample	\$740/sample	\$540/sample
Annual Costs	\$7.98M	\$1.08M	\$1.45M	\$1.08M

* FY96 222-S laboratory volume



Cost Conclusions

- If LA/MS proves to be suitable to replace ICP/AES analysis and the 222-S laboratory throughput requirements remain as estimated, a maximum annual savings of \$7M in operating costs can be achieved if the technology is implemented.
- In addition to the labor, turn around time, and throughput advantages provided by the LA/MS method, it also can provide the required analytical data with reduced radiation exposures for analytical staff because the samples do not need to be transferred outside the hot cell for dissolution and analysis.
- The effectiveness of the LA/MS technique over that of ICP/MS has been shown. For each criteria examined (e.g., Throughput, Labor Hours, or Elapsed Time) the LA/MS method provides significant advantages for the analysis of solid samples. LA/MS data collection/reduction only takes approximately two hours per sample.
- Indirect cost savings to the overall remediation program can result from the higher analysis throughput capability of the LA/MS method. During high laboratory load periods, the LA/MS method can minimize overall process delays which might result if decisions were delayed until data were available. In some cases, slow data availability can become the pace setter for an overall system that was designed for much higher throughput. These indirect savings have not been considered in these cost/time analyses.
- Several issues pertinent to a “complete” comparison have not been dealt with in this report because they depend on application specific information and can not be dealt with in a generalized comparison. An example of such an item is intra- and inter- facility sample movement. However, incurred delays from such movements will affect the baseline method far more than LA/MS, since the analytical procedure for the latter can be done in one location (the baseline method requires two sample transfers).



SECTION 6

REGULATORY AND POLICY ISSUES

Regulatory Considerations

No regulatory/policy issues have been identified for the application of the LA/MS technology except those associated with

- working with radioactive sample materials
- working with energetic, industrial laser systems.

Clear guidelines and procedures exist at DOE sites and numerous other industrial sites for work involving both of these industrial hazards.

Radiation Safety Efforts for Hot Cell LA/MS System Deployment

The LA/MS instrument system design, including the fume hood enclosure for the ICP/MS, fully meet the design criteria established by WHC and KHC staff. Fume hood design and hot cell modifications were chosen to ensure radiation safety compliance while enabling effective operation and maintenance. The ICP/MS operating in the fume hood presents no new safety issues beyond those routinely dealt with for numerous ICP/AES instruments operating elsewhere in the 222-S laboratory. Fume hood exhaust was fully integrated into the overall laboratory exhaust and HEPA filtration system.

Laser Safety Efforts for Hot Cell LA/MS System Deployment

The LA/MS laser source and beam transfer system were designed with interlocked safety covers and shields to allow system operation under Class I laser safety guidelines when all shields are in place. When shields are removed, the laser safety interlocks automatically prevent laser operation.

Laser curtains were incorporated in the system design to allow laser source alignment and servicing on the hot cell roof under more restrictive safety guidelines. Under these conditions, access to the hot cell roof area is controlled under criteria for operation of a Class IV laser system. All staff in the area must have appropriate laser safety training, wear appropriate laser safety equipment, and follow the laser safety procedures specified for servicing the system laser.

Staff in the remainder of the hot cell laboratory (i.e., outside the laser safety curtains) can operate without restrictions associated with the LA/MS system laser operation.



SECTION 7

LESSONS LEARNED

Implementation Considerations

- Equipment costs for a new application will depend on application specific requirements that may include ICP/MS containment in a glove box (compared to the fume hood employed at Hanford) and reduced auxiliary instrumentation suite (compared to the full suite employed at Hanford). Site requirements will govern the actual cost.
- A “Method Validation” phase has not been conducted yet. Method Validation would include testing the new method to a sufficient level in order to establish (positive or negative) that the method results correlate sufficiently with the baseline method. When this validation is completed successfully, the new method may be implemented immediately with minimal technical risk to the user program.
- An analytical chemist or technical specialist can perform system operation. With current software, a chemist must perform data reduction and analysis. When data reduction improvements currently under development are implemented, technical specialists can perform much of the preliminary processing with final interpretation by a chemist.

Technology Limitations and Needs for Future Development

- There are no outstanding scale-up requirements for the basic LA/MS system equipment either for other DOE applications/sites or for non-DOE applications. System operating conditions (e.g., laser pulse energy) may need to be revised for different applications, but the system design provides the capability to easily make these adjustments using system controls.
- Systems engineering/integration may be needed for certain applications to meet requirements for sample throughput or sample handling criteria (e.g., special equipment enclosures for carcinogens and radioactive materials).
- Method development should be carried to a point where the data could be processed to determine quantitative analytical results. This method refinement would result in method knowledge and data reduction software that could be deployed with an LA/MS system. Completing this task would significantly advance the overall capability of the method and the deployed technology.

Technology Selection Considerations

While initial equipment and system revision costs are important considerations that must be addressed when evaluating the usefulness of this technology, the current semi-quantitative nature of the LA/MS must be considered during any deployment assessment.



APPENDIX A

REFERENCES

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APPENDIX B

ACRONYMS AND ABBREVIATIONS

LA/MS	Laser Ablation/Mass Spectroscopy
ICP/AES	inductively coupled plasma/atomic emission spectroscopy
ICP/MS	inductively coupled plasma/mass spectrometry
LIBS	laser induced breakdown spectroscopy
OST	Office of Science and Technology
PNNL	Pacific Northwest National Lab
TFA	Tanks Focus Area
TWRS	Tank Waste Remediation System



